
Polymer Science Dictionary

Second edition

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atomic number <20), in contrast to the related technique of X-ray fluorescence analysis. The technique, with the related technique of electron microscopy for chemical applications, is useful for the identification of surface atoms and for depth analysis. Applications include the identification of thin layers of polymers, surface treatments and coatings and in surface degradation studies.

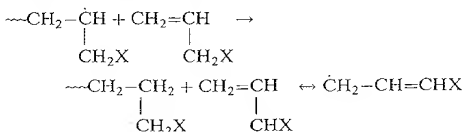
autoacceleration (*gel effect*) (*Tromsdorff effect*) (*Tromsdorff-Norrish effect*) An increase in the rate of a free radical polymerization with an increase in conversion. It is due to the increasing viscosity of the monomer/polymer mixture and/or occlusion of growing active centres, causing a decrease in the mobility of the growing active centres, which in turn slows termination. The effect is most pronounced in concentrated systems, such as in mass polymerization, especially if the monomer is a poor solvent for the polymer, and in solution polymerization in poor solvents.

autocorrelation function In photon correlation spectroscopy, a function of the photon count (light intensity i_0 measured at angle θ), defined as $G'(\tau) = \lim [1/T \int i_0(t) i_0(t+\tau) dt]$, where $i(t+\tau)$ is the scattered light intensity after a variable time delay of τ and T is the experimental time. The decay of its normalized value $G'(\tau) = G'(\tau)/G'(0)$, where $G'(0)$ is the time averaged value of the square of the intensity $\langle i_0(t)^2 \rangle$, gives information on the molecular motions of polymer molecular scatterers in solution. The function is determined by counting photons with a photomultiplier during short time intervals Δt . The photon counts are then evaluated in an autocorrelator (a computer chip), which evaluates the product $i(t)i(t+n\Delta t)$ after various (n) time intervals of $t+n\Delta t$.

autocorrelator A computer device which calculates the autocorrelation function in photon correlation spectroscopy by calculating the product $i(t)i(t+n\Delta t)$ from the scattered photon counts, where $i(t)$ is the light intensity after time t and $i(t+n\Delta t)$ after various time intervals $t+n\Delta t$.

autohesion Alternative name for *tack*.

autoinhibition Inhibition of free radical polymerization when the monomer itself is the inhibitor. This results in a low polymerization rate and the formation of only low molecular mass polymer. It occurs with allylic monomers (of the type $\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}_2\text{X}$) as a result of degradative chain transfer since the C-H bond α to the double bond (the allylic hydrogen) is weak. In addition, the allyl radical produced is highly resonance stabilized. The reaction is thus an allylic abstraction reaction with chain transfer to monomer:



The allyl radical produced is too stable to re-initiate polymerization, so inhibition has occurred.

automated image analysis (AIA) A technique for the analysis of a transmission electron microscopy micrograph, using a variable light spot to measure particle diameter by comparison with standard reference micrographs, and automatically recording the values.

autoorientation mechanism A mechanism which explains the spherulitic mode of crystallization, whereby a crystallite is formed and then induces formation of a neighbouring crystallite oriented perpendicularly to it. The process repeats itself to produce a herringbone-like array of crystallites, eventually growing into a spherulite.

autooxidation Free radical oxidation by atmospheric oxygen in which the products catalyse further oxidation and therefore cause an acceleration in the oxidation rate. Usually hydroperoxides are responsible since they dissociate either thermally or on ultraviolet light irradiation to free radicals which initiate new oxidation chains. The progress of autooxidation is measured, for example, by oxygen uptake and shows an induction period followed by the autoacceleration stage.

AV Abbreviation for *acid value*.

average functionality Symbol f_{av} . In a step-growth polymerization when a mixture of monomers of different functionality is used, the average functionality is the average number of functional groups per monomer molecule, for all types of monomer molecules, i.e. $f_{av} = \sum N_i f_i / \sum N_i$, where N_i is the number, or number of moles, of monomer with functionality f_i . f_{av} is used in the Carothers equation for non-linear polymerization in predicting the critical conversion for gelation.

average molar mass (*average molecular mass*) (*molar mass average*) (*molecular mass average*) (*molecular weight average*) Symbol \bar{M} . The molecular mass of a polymer sample that results from one of several possible methods of averaging of the different molecular sizes present in polymer samples that are not monodisperse. Since polymerization is a random process, most polymer samples contain a range of molecular sizes (given by the molecular mass distribution), i.e. they are polydisperse, so some molecular mass average must be used. Several different averages, all ratios of the moments of the distribution, are used. They are given by

$$\bar{M} = \sum_i N_i M_i^{n+1} / \sum_i N_i M_i^n$$

where there are N_i molecules of molecular mass M_i for each molecular species i . In the number average molecular mass (\bar{M}_n), $n=1$, in the weight average molecular mass (\bar{M}_w), $n=2$, in the z-average molecular mass (\bar{M}_z), $n=3$, in the z+1-average molecular mass (\bar{M}_{z+1}), $n=4$, etc. \bar{M}_n is the most sensitive average to low M_i species and as we go to \bar{M}_w to \bar{M}_z to \bar{M}_{z+1} , etc. the average becomes more sensitive to molecules with high M_i . The viscosity average molecular mass

and the sedimentation-diffusion average molecular mass are of a slightly different type. The average molecular mass is related to the average degree of polymerization by $\bar{M} = M_0 \times \overline{DP}$, where M_0 is the molecular mass of the repeat unit and \overline{DP} is the average degree of polymerization.

The polymerization conditions control the molecular mass of the polymer produced. In step-growth polymerization high fractional conversions (p) are needed for high molecular mass, since $\bar{x}_n = 1/(1-p)$ for simple linear polymerization, where \bar{x}_n is the number average degree of polymerization. In chain polymerization the polymer molecular mass decreases with increasing temperature, transfer and termination. Hence to achieve the desirable high molecular masses often needed, strict control over the reaction conditions is necessary. If too high a molecular mass results, then a modifier may be used.

A wide range of molecular masses is found in synthetic polymers; values of a few hundred (in oligomers), a few thousand (in prepolymers, which are often subsequently chain extended), several thousand to about 20 000 (common in synthetic fibres), 20 000 to 100 000 (common in plastics and some rubbers) and several million (in some other rubbers). Crosslinking greatly increases molecular mass and heavily crosslinked molecules (network polymers) have molecular masses approaching infinity. Biopolymers, which are often monodisperse, have molecular masses ranging from a few hundred (some simple proteins and polysaccharides) to hundreds of million (nucleic acids).

The value of the molecular mass average is frequently the most important structural feature, apart from the repeat unit structure, especially since the mechanical properties are molecular mass dependent. Generally in the range 10^3 – 10^4 , a polymer is mechanically weak (soft or brittle solid), whereas above 10^5 little improvement in these properties occurs. Thus many polymers for use as plastics, rubbers, fibres, adhesives and coatings have molecular masses of 10^4 – 10^5 . As molecular mass increases, so melt viscosity increases, and melt processing becomes more difficult.

Many techniques are used to determine molecular mass averages. Usually a particular method yields only one average. Thus colligative property methods (vapour pressure lowering, cryoscopy, ebulliometry, osmometry) yield \bar{M}_n , dilute solution viscometry yields \bar{M}_v , light scattering yields \bar{M}_w and sedimentation can yield \bar{M}_n , \bar{M}_w and \bar{M}_z . Values for all the averages can be obtained by gel permeation chromatography.

average molecular mass Alternative name for *average molar mass*.

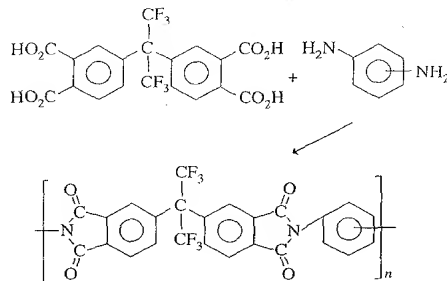
average molecular weight Alternative name for *average molar mass*.

Avimid Tradename for a high temperature resistant polyimide.

Avimid K-III Tradename for a polyimide which is amorphous. It has a T_g of 251°C and is produced by

reaction of an aromatic tetracarboxylic anhydride or half-ester with an aromatic diamine. Useful as an adhesive and laminating resin.

Avimid N Tradename for a polyimide containing hexafluoroisopropylidene groups, produced by reaction of phenylenediamine with a fluorodianhydride, of structure:



containing about 95% *para*- and about 5% *meta*-phenylenediamine links. It has a T_g of about 325°C, is oxidatively very stable and is useful as a composite laminating resin.

Avlin Tradename for a *viscose rayon* staple fibre.

Avrami equation A relationship expressing the dependence of the amount of a crystallizing polymer that has crystallized with time, i.e. a crystallization rate equation. Its most general form is

$$W_L/W_0 = \exp(-Kt^n)$$

where W_L and W_0 are the masses of melt at time $t = t$ and $t = 0$ respectively, K is a rate constant and n is the Avrami exponent. Ideally n has an integer value which is the sum of the number of dimensions in which growth has taken place (three for spherulites, two for discs and one for rods or fibrils) and of the order of the time dependence of the nucleation process. This latter is either unity for sporadic nucleation (where the number of nuclei increases linearly with time) or zero (instantaneous nucleation). Thus for the frequently observed spherulite growth from sporadic nucleation, $n = 3 + 1 = 4$. In practice experimental data often give non-integral values of n due to the simultaneous operation of different growth processes.

Avril Tradename for a crosslinked *viscose rayon* with a high tenacity of 3.2 g denier⁻¹ (dry), 2.2 g denier⁻¹ (wet) and about 10% elongation at break.

Avron Tradename for a medium tenacity *viscose rayon*.

axial correlation A correlation along the direction of a polymer chain, particularly referring to orientation in the chain direction, where the repeat units are linearly correlated.